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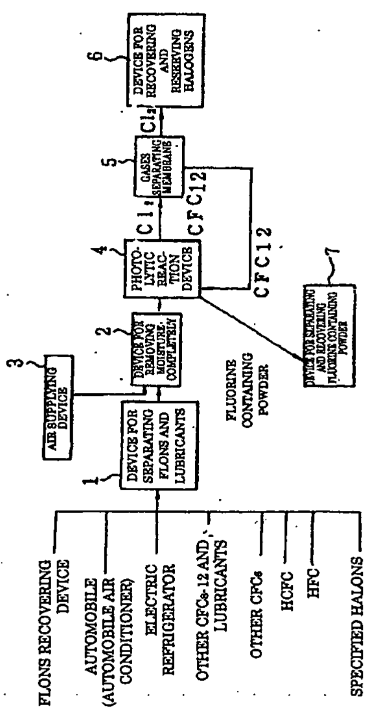
(54) Title of the Invention: APPARATUS FOR DECOMPOSING AND RECYCLING FLONS AND THE LIKE BY ULTRAVIOLET LIGHT AND METHOD THEREOF

(57)[Abstract]

[Object] The object of the present invention is to establish a system for uninterruptedly decomposing and recycling flons and the like by ultraviolet light, and to put the system into practical use.

[Constitution] Recovered flons and the like (e.g. specified frons, alternative flons, halons and halogenated organic solvents) are decomposed and are rid of lubricants by a device 1 for separating flons and lubricants at a room temperature and under a normal pressure. Hereafter, moisture which is a factor in inhibiting flons and the like from being decomposed by ultraviolet light is completely separated in a device 2 for removing moisture completely while being supplied with air by an air supplying device 3. The flons are decomposed by a photolytic reaction device 4, and then produced gases which contain chlorine as a main component are separated by a gases separating membrane 5. Thence, the chlorine is recovered by a device 6 for recovering and reserving halogens, and unreacted flons are recovered into the photolytic reaction device 7 where the unreacted flons are once more subjected to a photolytic reaction process. In a case that bromine is contained, unreacted halons are separated by a gas-liquid separation method. Fluorine containing powder which is a product made by a photolytic reaction is recovered by a device 7 for separating and recovering fluorine containing powder.



[Scope of Claim]

[Claim 1] A method for decomposing and recycling flons and the like by ultraviolet light, which adds air, as an accelerator for a photolytic reaction, to at least more than one kind of flon or the like out of specified flons, alternative flons, halons and halogenated organic solvents, and which decomposes the flon(s) or the like photolytically by ultraviolet light, and which separates solid products and halogenated products, and which makes them harmless, the method being characterized in that the flons and the like which are supplied uninterruptedly are processed in a way that the flons and the like are separated from and rid of lubricants at a room temperature and under a normal pressure, and the flons and the like which have been rid of lubricants and the air are rid of moisture completely, and the flons and the like are photolyzed by ultraviolet light, and halogenated compounds are separated and recovered from the products.

[Claim 2] An apparatus for decomposing and recycling flons and the like by ultraviolet light, which adds air, as an accelerator for a photolytic reaction, to at least more than one kind of flon or the like out of specified flons, alternative flons, halons and halogenated organic, and which photolyzes the flon(s) or the like by ultraviolet light, and which separates solid products and halogenated products, and which makes them harmless, the apparatus comprising: a device for separating gases from liquids, adapted for the flons and the like, which causes the flons and the like to be separated from and rid of lubricants at a room temperature and under a normal pressure; a device for supplying air which is to be added as an accelerator for a photolytic reaction; a device for removing moisture completely which causes moisture to be completely separated and removed from the flons and the like as well as the air which have been supplied from the two aforementioned devices; a photolytic reaction device equipped with a unit for irradiating ultraviolet light, which introduces the flons and the like which have been rid of the moisture completely; a separator for separating gaseous and liquid halogenated compounds which have been produced by the photolytic reaction; and a device for separating and recovering halogens which recovers the halogenated compounds which have been separated by the separator, and wherein the flons and the like which are supplied uninterruptedly are processed by use of each of the aforementioned devices.

[Detailed Description of the Invention]

[0001]
[Industrial Field to which the Invention is applicable] The present invention relates to a method for decomposing and recycling specified flons (hereinafter referred to as "CFCs" in some cases) as well as flon equivalents such as halons, alternative flons (HCFC,HFC) and halogenated organic solvents (hereinafter, the aforementioned substances are referred to as "flons and the like," including the specified flons, in some cases), specifically to a system for decomposing and recycling the flons and the like by use of ultraviolet light with efficiency.
[0002]
[Prior Art] CFCs which are used in freezers, refrigerators, air conditioners, aerosols, and detergents and the like for cleaning electronic parts or for dry cleaning are emitted into the atmosphere, rise up to the stratosphere, and are photolyzed by the solar light there. It is said that free-chlorine atoms produced in this way destroy the ozone layer. There is a research report which estimates that the cross-sectional area for absorbing infrared ray for each CFC molecule is nearly a hundred times larger than that for each CO_2 molecule, and that the global warming effect for each CFC molecule is up to 10,000 to 20,000 times larger than that for each CO_2 molecule. Against this background, necessity for reduction in the amount of CFCs for use is claimed for. Present measures to be taken for reduction in CFCs are twofold: a method of suppressing the emission of CFCs into the atmosphere and a method of replacing CFCs with alternatives. The method of suppressing the emission of CFCs into the atmosphere is divided into (a) a method of recovering and recycling CFCs and (b) a method of decomposing CFCs. Since it is a practical measure to decompose used CFCs, a variety of methods for decomposing flons have been under consideration. However, none of the methods has not been put into practical use.
[0003] In the 1992 Meeting of the Parties to the Montreal Protocol which is a treaty of regulation on substances which depletes the ozone layer, a complete phase out of the production of HCFCs by 2020 was determined as a general rule. On the other hand, HFCs do not destroy the ozone layer. However, since HFCs have a global warming effect, it is assumed that some regulations will be introduced in the future. In addition, in particular with regard to HCFC-22 which has already been used for household air conditioners and the like for nearly 20 years, and which is sill domestically

produced in an annual amount of more than 30,000 tons, an issue of processing HCFC-22 so as to make it harmless has arisen as an important issue second to the CFC issue. If, therefore, alternative flons such as HCFCs and HFC can be processed so as to make them harmless, this can contribute to the protection of the global environments. The present inventors have previously developed a method for uninterruptedly decomposing and separating flons, which decomposes flons by irradiating ultraviolet light, which has a specific wavelength which attains the highest decomposing rate, to gaseous flons which are supplied uninterruptedly, and for uniterruptedly separating reacted products and unreacted flons by a separating membrane, and an apparatus for which the method is adapted, and they have filed patent applications (Tokugan Hei.No.3-306297 and Tokugan Hei.No.4-137311).

[0004]

[Problem to be Solved by the Invention] The aforementioned invention for which the present inventors have filed the patent applications relates to a method for uninterruptedly decomposing and separating flons without a chemical process and an apparatus for which the method is adapted. However, the invention has not established a system, for decomposing and recycling flons, which includes recovering flons which are used in various fields of application, supplying the recovered flons to the aforementioned process for uninterrupted decomposition and separation, and recovering products which are made by decomposing the flons. Therefore, the object of the present invention is to establish a system for decomposing and recycling flons and the like by use of ultraviolet light, and to put the method into practical use.

[0005]

[Means for Solving the Problems] The aforementioned object of the present invention is attained by the following constitution. In other words, the constitution includes a method for decomposing and recycling flons and the like by ultraviolet light. The method adds air, as an accelerator for a photolytic reaction, to at least more than one kind of flon or the like out of specified flons, alternative flons, halons and halogenated organic solvents, and photolyzes the flon(s) or the like by ultraviolet light, and separates solid products and halogenated products, and makes them harmless. In the method, flons and the like which are supplied uninterruptedly are processed

in a way that the flons and the like are separated from and rid of lubricants at a room temperature and under a normal pressure, and the flons and the like which have been rid of lubricants and the air are rid of moisture completely, and the flons and the like are photolyzed the ultraviolet light, and halogenated compounds are separated and recovered from the products, or

[0006] An apparatus for decomposing and recycling flons and the like by ultraviolet light, which adds air, as an accelerator for a photolytic reaction, to at least more than one kind of flon or the like out of specified flons, alternative flons, halons and halogenated organic solvents, and which photolyzes the flon(s) or the like by ultraviolet light, and which separates solid products and halogenated products, and which makes them harmless. The apparatus comprises: a device for separating gases from liquids, adapted for the flons and the like, which causes the flons and the like to be separated from and rid of lubricants at a room temperature and under a normal pressure; a device for supplying air which is to be added as an accelerator for a photolytic reaction; a device for removing moisture completely, which causes moisture to be completely separated and removed from the flons and the like as well as the air which have been supplied from the two aforementioned devices; a photolytic reaction device equipped with a unit for irradiating ultraviolet light, which introduces the flons and the like which have been rid of the moisture completely; a separator for separating gaseous and liquid halogenated compounds which have been produced by the photolytic reaction; and a device for separating and recovering halogens which recovers the halogenated compounds which have been separated by the separator. In the apparatus, the flons and the like which are supplied uninterruptedly are processed by use of each of the aforementioned devices.

[0007] The previous invention for which the present inventors have file the patent application reported that a wavelength most suitable for decomposing specified flons was around 190nm. However, a performance of a low pressure mercury lamp which was used at that time made it impossible for the mercury lamps to output wavelengths which were shorter than 185nm. As a consequence, it is probable that a wavelength which can decompose flons and the like with highest efficiency for the present invention is shorter than 185nm. Examples of specified flons (CFCs) which are decomposed according to the present invention are CFC-11(CCl_3F), CFC-12(CCl_2F_2),

$CFC113(CCl_2F\text{-}CClF_2)$, $CFC\text{-}114(CClF_2\text{-}\ CClF_2)$, $CFC\text{-}115(CClF_2\text{-}CF_3)$. What are defined as flon equivalents in the present invention are halons (1211:CF_2ClBr, 1301:CF_3Br, 2402:CF_2BrCF_2Br), alternative flon HCFCs (22:CHF_2Cl, 123:$CHCl_2CF_3$, 141b:CH_3CCl_2F), an alternative flon HFC (C134a:CH_2FCF_3) and halogenated organic solvents (carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene) and the like. Incidentally, a wavelength of an ultraviolet lamp used for HFCs needs to be different from that used for the other compounds.

[0008] According to the present invention, recovered flons and the like are separated from and rid of lubricants from which harmful sunstances will likely be produced by irradiation of ultraviolet light of a room temperature and under a normal pressure, and are subjected to a photolytical reaction. In this point, oxygen in the air is used as an accelerator for the photolytical reaction. By using air as a source from which oxygen is obtained, the oxygen can be an inexpensive accelerator. In addition, if moisture is entrained in a photolytic reaction device, hydrogen fluoride which is harmful to human bodies is produced in the course of a photolytical reaction. For this reason, flons and air which are completely rid of moisture need to be introduced. Chlorine (in a case of flons, and 1,1,1-trichloroethane) and bromine (in a case of specified halons) which are produced through a photolytical reaction can be removed by a separating unit such as a gases separating membrane easily, and can be reserved into a recovering and reserving device. In addition, since fluorine containing powder which is produced through the photolytical reaction is solid, the fluorine is separated from the potolytical reaction device, and is recovered into a recovering device.

[0009] A principle of the processing method is to efficiently conduct in a reaction container on the earth a halogen atomic photodissociation reaction by ultraviolet light on flons and the like which occurs in the ozone layer. For this reason, ozone layer destroying substances can be so processed to be made harmless by this method.

(Analysis and estimation of a decomposition reaction by use of ultraviolet light employed in a method of molecular orbitals) In the patent application previously filed by the present inventors, an analysis of a decomposition reaction of CFCs by use of ultraviolet light was calculated through a method of molecular orbitals (PM3) by a personal computer, thereby estimating the

followings.

[0010] (i) When the strengths of C-Cl bond, C-F bond and C-C of 5 types of CFCs and a CFC radical were calculated, approximately 10eV was obtained for C-Cl bond, approximately 14.5eV for C-F bond, and approximately 12ev for C-C bond, in spite of the difference between the 5 types of CFCs and the CFC radical (a chlorine dissociation radical). For this reason, if wavelengths of ultraviolet light is limited, it is highly likely that only C-Cl bond, which is the smallest in bond energy, can be photolytically dissociated (see Table 1).

(ii) Potential curves of photolytical reactions (Cl dissociations) of the 5 types of CFCs and the CFC radical show that the potential curves of the 5 types of CFCs and the CFC radical reaction cross over a dissociation curve of chlorine in the vicinity of minimum points of the respective excitation states, and that the 5 types of CFCs and the CFC radical dissociate a chlorine atom by specific ultraviolet light.

[0011] In the present invention, it has been confirmed by a method of molecular orbitals in mathematical chemistry (a calculation by a method of molecular orbitals (PM3) by use of a personal computer MOPAC/386(corresponding to Version 6.0, manufactured by To-ray System Center, Inc.) and by a MOPAC Version 6.01 (Japan Chemical Program Exchange JCPE Program P015, for a large scale computer)) that the HCFCs can be photolyzed by a wavelength which is nearly as long as that of the CFCs, as in the case of the previously-mentioned patent application.

[0012] The following conclusions have been obtained by the reaction analysis and the reaction estimation by use of ultraviolet light which have been conducted this time.

(i) Ozone layer destroying substances are subjected to a common photolytical reaction. A photolytical reaction has been considered for ozone layer destroying substances other than specified flons shown in Table 2, such as specified halons, HCFC alternative flons and halogenated organic solvents (although HFC134a and 1,1,1-trichloroethylene are not ozone layer destroying substances, considerations have been given to them for a comparative purpose). As a result, it has been assumed that ozone layer destroying substances including specified flons can be subjected to a common photolytical reaction.

[0013] a. Wavelengths suitable for the photolytical reactions take up

values approximate to each other.

[Table 1]

EXCITATION ENERGY NEEDED FOR PHOTOLYTIC REACTION OF SPECIFIED FLONS*

KINDS OF SPECIFIED FLONS	CFC11 (CCl_3F)	CFC12 (CCl_2F_2)	CFC113 (CCl_2F-$CClF_2$)	CFC114 ($CClF_2$-$CClF_2$)	CFC115 ($CClF_2$-CF_3)
EXCITATION ENERGY	85.17	84.10	83.34	80.41	78.40

$*R \rightarrow R\cdot + Cl\cdot$ UNIT: kcal/mol

[0014]

[Table 2]

FLON EQUIVALENTS		CONSTITUTIONAL FORMULAE	EXCITATION ENERGY (kcal/mol)
HALONS	1211	CF_2ClBr	73.23
	1301	CF_3Br	64.86
	2402	CF_2BrCF_2Br	74.64
(ALTERNATIVE FLONS) HCFC	22	CHF_2Cl	82.15
	123	$CHCl_2CF_3$	68.42
	141b	CH_3CCl_2F	64.08
HFC	134a	CH_2FCF_3	163.82
ORGANIC SOLVENTS	CARBON TETRACHLORIDE	CCl_4	66.59
	TRICHLOROETHANE	CH_3CCl_3	73.20
	TRICHLOROETHYLENE	$ClHC{=}CCl_2$	107.41

[0015] b. A bromine atom is dissociated from each of the specified halons, and a chlorine atom is dissociated from the specified flons, HCFC alternative flons and organic solvents.

c. When a photodissociation potential curve crosses over a dissociation potential curve of T_1(minimum excitation triplet state) halogen atom in the vicinity of a minimal point of its S_1 (minimum excitation-multiplet state), the photodissociation dissociates a halogen atom.

d. As an experiment for a comparative purpose, HFC134a was photolyzed, and it was found that HFC134a can be photolyzed by ultraviolet light. In the photolytical reaction, a dissociation reaction of C-C bond occurs, and a halogen atom is dissociated directly from S_1. In addition, the most suitable dissociation wavelength is on the side of short wavelengths in relation to halves of wavelengths of ozone layer destroying substances. For this reason, a source of light different from those of other substances needs to be chosen.

e. In a photolytical reaction of trichloroethylene which was carried out for a comparative purpose, a dissociation of C=C bond occurred. In addition, the most suitable dissociation wavelength is on the side of short wavelengths in relation to ozone layer destroying substances.

[0016] (ii) Specified halons and HCFC alternative flons is subject to a specified atom extraction reaction which is caused by an oxygen radical or the like. With regard to specified halons and HCFC alternative flons, specified atom extraction reactions caused by oxygen atom radicals and chlorine atom radicals have been put under consideration by using a simulation model shown in Fig.2. As a result, it was found that, as in the case of the specified flons, the specified halons and HCFC alternative flons are subject to extraction of a chlorine atom and a hydrogen atom in the molecules by an oxygen atom radical, a chlorine atom radical and a bromine atom radical.

From the results of the aforementioned (i) and (ii), it is found that the method according to the present invention is not only a method for making flons harmless and recycling them by use of ultraviolet light (by use of oxygen as a reaction accelerating gas), but also a method which subjects other ozone layer destroying substances to a process for making them harmless and recycling them (by use of oxygen as a reaction accelerating gas) by use of ultraviolet light by choosing suitable gases separating membranes.

[0017]

[Examples] An embodiment according to the present invention will be described with reference to drawings. In this embodiment, the description will be provided for a process for recovering, decomposing and recycling flons,

which are representative of flons and flon equivalents, unless otherwise specified. Fig.1 is a schematic block diagram of a system for decomposing and recycling flons by use of ultraviolet light according to the present embodiment. Various flons recovered are rid of, and removed from, lubricants by a device 1 for separating flons and lubricants. Then, in order to completely separate moisture which is a factor of inhibiting decomposition of the flons by ultraviolet light, the flons are introduced to a device 2 for removing moisture completely. The air which is a reaction accelerating gas is introduced from an air supplying device 3, and moisture is removed through the device 2 for removing moisture completely. Hereafter, the flons are decomposed in a photolytical reaction device 4. Gases whose chief components are chlorine gases thus produced (in a a case of halons, bromine can be easily separated from gases and recovered since the bromine is liquid (the boiling point of bromine is 58.8°C)) are separated by a gases separating membrane (in the case of bromine, a membrane is not needed). Chlorine (or bromine) is recovered by a device 6 for recovering and reserving halogens, and concurrently unreacted flons (halons) which have been separated by the gases separating membrane are recovered into the phololytical reaction device 4, where the flons (halons) are once more subjected to a photolytical reaction. Furthermore, fluorine containing powder which has been produced by the photolytical reaction are recovered into a device 7 for separating and recovering fluorine containing powder.

[0018] (1) The device 1 for completely separating flons and lubricants which are contained in refrigerants.

Refrigerants used in an automobile air conditioner and an electrical refrigerator are composed of CFC-12 and lubricant with a weight ratio of 1:1. As the lubricants, mineral oil containing lubricants, including aromatic carbon hydride containing lubricants, are used.

(A reaction analysis and a reaction estimation of lubricants by a method of molecular orbitals)

Lubricants used in compressors of an electrical refrigerator and an automobile air conditioner are composed of naphthenic, paraffin and aromatic oils. For this reason, prior to an experiment, photolytical properties of each constituent ingredient of the naphthenic, paraffin and aromatic oils are calculated through the method of molecular orbitals (PM3) by the large scale computer and the personal computer, and the following

results are obtained.

[0019] a. Photoexcitation energy for naphthenic and paraffin lubricants (dissociation of a C-H bond) needs to be over twice more energy of a 185nm wavelength of the shortest ultraviolet light to be used for a low pressure mercury lamp (ultraviolet light of a short wavelength which is shorter than the half). For this reason, naphthenic and paraffin lubricants are not photolyzed by a low pressure mercury lamp.

b. It is possible that with regard to aromatic lubricants, the C-H bond is photolyzed by the 185nm wavelength of a low pressure mercury lamp. In addition, when a aromatic radical and a chlorine radical which is produced by a photolytical dissociation of the specified flons are bonded, it is likely that chemical compounds which includes strong toxicity are produced. For this reason, lubricants have to be removed completely before introduced into the photolytical reaction device 4. Out of the aromatic carbon hydrides, some cause a photolytical reaction by a wavelength of a low pressure mercury lamp or an ultraviolet light of a photolytical wavelength which is the most suitable for CFC-12, depending on their chemical constitutions (benzene:122.94kca/mol,toluene:122.45kcal/mol,isobutylbenzene:121.45kcal mol, naphthalene:103.80kcal/mol, β-isobutylnaphthalene:104.62kcal/mol). In addition, a chlorine radical which is produced by a photolytical reaction of CFC-12 or an oxygen atom which is produced by a photolytical reaction of oxygen (a reaction accelerating gas) causes a chemical reaction along with these aromatic carbon hydrides, it is likely that scores of types of compounds are produced. In particular, production of chlorine containing harmful matter such as dioxin and PCB is apprehended. For this reason, lubricants and CFC-12 need to be completely separated, and only CFC-12 needs to be introduced into the reaction device.

[0020] (A structure of the device 1 for separating flons and lubricants) It was found that, when CFC-12 and lubricants are placed at a room temperature and under a normal pressure, only CFC-12 can be taken out while in a gaseous state because of the difference between the boiling temperatures of CFC-12 and lubricants (CFC-12:-29.79°C, lubricants: higher than 250°C), and that accordingly the CFC-12 can be introduced into the photolytical reaction device 4 after being made harmless as purified. However, if the CFC-12 is taken out in a gaseous state at a room temperature, 5% of the CFC-12 remains in the lubricants. Since the

CFC-12 remaining in the lubricants is bonded with the lubricants not chemically but physically, the CFC-12 only can be taken out because of the difference in the boiling temperatures, if leaving the CFC-12 remaining lubricants at a temperature of 100°C to 200°C for about two hours.

[0021] With this taken into consideration, in order to put the separating device into practical use, the device 1 for separating flons and lubricants is configured to being provided with separators 10 in multiple steps. Introduction ducts 11 of refrigerants of an automobile air conditioner and an electrical refrigerator, which have been recovered by a flons recovering device are connected with the inlet of each separator 10. Then, composition of flons and a minute amount of sprayed lubricants are introduced through the inlet duct 11, and the CFC-12 and the lubricants are separated in a separator 10 at a room temperature and under a normal pressure. Separated flons are introduced from the outlet of the separator 10 to the inlet of a separator in the next step through the duct 11. A felt-like filter 12 is provided to a separator 10 in the vicinity of the outlet so that sprayed flons are aimed not to leak out along with the flons from the outlet. In addition, separated liquid lubricants are reserved in a lubricant reservoir 13 which is arranged at the bottom of the separators 10. In this point, in order to separate the lubricants from the flons completely, a baffle board 15 may be arranged in a position opposite to a direction in which mixture of flons and lubricants are blown into the separators 10 so that splash of the lubricants is intended to be prevented by blowing a flow of the introduced mixture onto the baffle board. In this manner, the recovered flons can be rid of lubricants completely by causing the mixture of the flons and lubricants passing through the multi-step separators 10.

[0022] (2) Decomposition of flons by ultraviolet light by use of the air as a reaction accelerating gas

Oxygen is used as a reaction accelerating gas for decomposition of flons by ultraviolet light. An oxygen molecule is photolyzed to produce oxygen atoms by ultraviolet light of a mercury lamp with a 185nm wavelength, in a way shown in the following reactio formula (1).

$$O_2 \rightarrow 2O\cdot \qquad (1)$$

It has been found by the method of molecular orbitals and the experimental results that this oxygen atom causes a reaction of extraction of a chlorine atom from flons, as shown in reaction formulae (2) and (3), and that

accordingly this oxygen accelerates decomposition of flons.
[0023]
[Chemical formulae]

$$\begin{array}{c} Cl \\ | \\ F\text{-}C\text{-}Cl \\ | \\ F \end{array} + \cdot O \rightarrow \begin{array}{c} Cl \\ | \\ F\text{-}C\cdot \\ | \\ F \end{array} + ClO \qquad (2)$$

$$\begin{array}{c} Cl \\ | \\ F\text{-}C\cdot \\ | \\ F \end{array} + \cdot O \rightarrow \begin{array}{l} F \\ \quad\diagdown \\ \qquad C: \\ \quad\diagup \\ F \end{array} + ClO \qquad (3)$$

If the air in the atmosphere can be used as it is for a source of supplying this oxygen molecule, the system according the present invention can be made simple and compact. For example, neither an oxygen cylinder nor a PSA (pressure swing adsorption) needs to be added to the processing apparatus. It was found by an experiment that there is no difference between pure oxygen and the air in terms of accelerating decomposition of flons.
[0024] (An experiment of producing nitrogen oxides by ultraviolet light under a condition that the air and flons co-exist) Ultraviolet light of a low pressure mercury lamp with a 185nm wavelength photolyzes an oxygen molecule, and produces oxygen atoms. In a case that the air is used as a source of supplying oxygen, it is apprehended that these oxygen atoms and a nitrogen molecule reacts with each other, nitrogen oxides which are harmful to human bodies are produced in accordance with a chemical formula (4).

$$N_2 + O\cdot \rightarrow N_2O \qquad (4)$$

Therefore, production of nitrogen oxides is put under consideration based on an experiment and mathematical chemistry. As a result, it was found that reactions expressed by the chemical formulae (2), (3) and (4) occur in a competitive manner, and that the reactions expressed by the chemical formulae (2) and (3) in an overwhelming manner while production of nitrogen oxides is made in a minute amount. The air and flons were mixed, and the mixture was introduced into a UV reaction unit. After ultraviolet

light was irradiated onto the mixture by two low pressure mercury lamps of 32W (a cold cathode type: manufactured by Rikokagaku, Inc.), an amount of nitrogen oxides (NOx) produced was measured by a measuring instrument. Results of this are shown below.

[0025]

[Table 3]

EXPERIMENTAL CONDITIONS

AIR (ml/minute)	CFC12 (ml/minute)	WITH OR WITHOUT UV LIGHT IRRADIATION	CONCENTRATION OF NOx (ppm)
1000	0	WITHOUT	0
1000	0	WITH	0
500	500	WITHOUT	0
500	500	WITH	0.2

It was found that an amount of NOx is 0.2ppm at a maximum as shown in the table, and that in particular production of NOx does not matter in the reaction of the mixture of the air and flons by ultraviolet light.

[0026] (3) The device 2 for removing moisture completely

When refrigerants are introduced into the photolytical reaction device 4, moisture which is included in the refrigerants is always is introduced the reaction device, too. In addition, when the air in the atmosphere is used as a reaction accelerating gas, moisture is also introduced into the reaction device along with the air. If the moisture is completely removed by a dehydrating device prior to introduction of the moisture into the reaction device 4, unnecessary harmful reactions expressed by the following chemical formulae are caused by moisture which is included in the reaction device.

$$H_20 \rightarrow H\cdot + OH\cdot \quad (5)$$

$$H_20 + O\cdot \rightarrow 2OH\cdot \quad (6)$$

$$CCl_2F_2 + H\cdot \rightarrow CCl_2F_2\cdot + HF \quad (7)$$

In particular, a reaction expressed by the chemical formula (7) produces hydrogen fluoride (HF) which is harmful to human bodies. In addition, this HF is transformed into hydrofluoric acid when moisture is present, and the hydrofluoric acid is such a harmful chemical compound as to corrode the

glass on the wall of the photolytical reaction device 4. Furthermore, a reaction of photolyzing water molecule by ultraviolet light expressed by the chemical formula (5) is a reaction of producing a hydrogen radical which is a cause of producing hydrogen fluoride. Moreover, a reaction expressed by the chemical formula (6) is an unnecessary reaction which consumes oxygen atoms which are chemical substances to accelerate a reaction of decomposing flons.

[0027] The device 2 for removing moisture completely according to the present embodiment is configured to have strong effect of moisture absorption which is obtained by providing a multiple of moisture absorption units (not illustrated) filled with moisture absorbent to a flons pathway and an air pathway which are located immediately before inlets for introducing the flons and air into the photolytical reaction device 4. Zeolite and calcium chloride are used as moisture absorbents, since they have a large effect of moisture absorption, and are harmless to human bodies, and are easy to handle. In this way, moisture which is included both in the air used as a reaction accelerating gas and flons which are separated from, rid of, lubricants is removed completely.

[0028] The device 4 for a photolytical reaction by ultraviolet light. In a case that the photolytical reaction device 4 is constructed of a glass container, ultraviolet light which is irradiated from an ultraviolet light generating unit which is arranged in the middle of the inside of the container permeates the glass and reach the outside of the glass. In addition, if the photolytical reaction device 4 is constructed of a container which is made of a metal, a high polymer molecule, a ceramic material and the like, ultraviolet light is absorbed by the container. Both of the aforementioned cases constitute a cause of reducing an energy effect in a photochemical reaction. Furthermore, ultraviolet light which permeates out of the glass container photolyzes oxygen in the air, and produces oxygen atoms which are harmful to human bodies and an ozone, as shown by the following chemical formulae (1) and (8).

$$O_2 \rightarrow 2O\cdot \qquad (1)$$

$$O_2 + O\cdot \rightarrow O_3 \qquad (8)$$

Moreover, the ultraviolet light which permeate out of the glass has a hazard of adversely affect a visual sensation.

[0029] With this taken into consideration, the photolytical reaction device 4

according to this embodiment is constructed of a glass reaction container 20 as shown in Fig.4. A plurality of ultraviolet lamps 21 are arranged in the inside of the glass reaction container 20. A outer periphery of the glass container 20 is covered by an ultraviolet light reflection membrane 22, and hereby ultraviolet light 23 which is irradiated from ultraviolet lamps 21 is reflected by the outer periphery of the glass container 20. In this way, an energy efficiency in the photolytical reaction is improved. In addition, harmful gases are prevented from being produced, and a visual sensation is protected.

[0030] An ultraviolet light reflection membrane 22 may be coated on either the inner side or the outer side of the outer periphery of the glass reaction container 20. In particular, a vacuum-deposited aluminium membrane is a preferable reflection membrane, since the membrane has a superb reflection rate (91.5% in a case of a 220nm wavelength) in the ultraviolet light range. In addition, the ultraviolet light reflection membrane 22 and the glass reaction container 22 which is coated with the reflection membrane 22 need to be in a close contact. A reason for this is that in a case that the ultraviolet ligt reflection membrane 22 is coated onto the surface of the outer wall of the glass reaction container 20, if there is an interval between the reflection membrane 22 and the wall surface of the glass reaction container 20, a photochemical reaction of oxygen in the air occurs, and the ultraviolet light is consumed so that oxygen atoms which are harmful to human bodies and an ozone are produced. If the ultraviolet light reflection membrane 22 is coated onto the surface of the inner wall of the glass reaction container 20, an oxide or a chloride is produced on the metal surface of the reflection membrane 22 by oxygen atoms and a chlorine radical which are products of the reaction. This reduces the reflection rate. Moreover, in a case that the material of the photolytical reaction device 4 is a synthetic quartsz which absorbs less ultraviolet light out of glasses, absorption of ultraviolet light always occurs in the glass of the outer periphery. This leads to loss of ultraviolet light. For this reason, it is preferable that a material which is made of LiF, CoF_2, a fused crystal or the like is used since they virtually absorb no ultraviolet light.

[0031] The method for decomposing and processing flons according to this embodiment is a method for processing flons to make them harmless by a gas phased photochemical reaction. In a case that a low pressure mercury lamp

of a cold cathode type (e.g. a lamp manufactured by Rikoukagaku, Inc.) is used as a source of light in the glass reaction container 20, tens of lamps with 100w as a maximum wattage are necessary. Since lives of mercury lamps differ from one to another, old lamps have to be replaced with brandnew lamps one by one. For this reason, a system for replacing and removing an ultraviolet lamp 21, which satisfies the following two conditions, is needed.

① The photolytical reaction container 20 is divided into two sections. One is a section of light source where ultraviolet lamps 21 are arranged. The other is a reaction container where ultraviolet lamps 21 are not arranged, where a mixed gas of flons and the air is supplied and exhausted.

② The section of light source and the reaction container are independent of each other. Replacement and removal of ultraviolet lamps in the section of light source can be performed without suspending the reaction even in the course of an operation.

③ Exchange and removal of ultraviolet lamps can be performed with ease.

[0032] To this end, according to this embodiment, the photolytical reaction device 4 adopts a type in which the section 20a of light source and the reaction container 20b have the respective mechanisms which are independent of each other as shown in Fig.5, and where the section 20a of light source and the reaction container 20b are connected with each other by optical fiber cables ((a) and (b) in Fig.5) or a high reflectance mirror ((c) in Fig.5). The section of light source is filled with a nitrogen gas or the like which does not absorb ultraviolet light. In addition, a condenser lens is arranged in the vicinity of the outlet from which ultraviolet light goes out in the section 20a of light source, and hereby ultraviolet light is supplied to the reaction container 20b efficiently. A schematic view of the device 4 as a whole shown in Fig.5 illustrates a case that the section 20a of light source in which ultraviolet lamps 21 are included and the reaction container 20b are connected with each other by the optical fiber cables 25. As shown in magnified views of connecting portions of the section 20a of light source and the reaction container 20b in Fig.5, each of the outer walls of the section 20a of light source and the reaction container, both of which are constructed of synthetic crystal glass, is coated by a high reflectance membrane 22 made of aluminium. By this, ultraviolet light from the section 20a of light source is irradiated onto the reaction container 20b efficiently, and ultraviolet light is evenly reflected from the outer wall of the reaction container 20b.

Accordingly, conditions for decomposition reactions of flons inside the reaction container 20b are made uniformly. Moreover, Fig.5 shows a magnified view of the aforementioned connecting portion to be adopted in the case that the section 20a of light source and the reaction container 20b is connected with each other by use of the high reflectance mirror 26. Ultraviolet light from the section 20a of light source is irradiated to the reaction container 20b, while reflected by the high reflectance mirror 26, from a connecting tube 27 which is filled with a nitrogen gas, and which is constructed of a material such as a metal or fluorine containing resin which does not absorb light of the low pressure mercury lamp.

[0033] In addition, as shown in Fig.6 (Fig.6(a) is a top view of the reaction container, and Fig.6(b) is a partial cross-sectional view of the side of the reaction container: the connecting portions of the section of light source and the reaction container 20 are not illustrated), a position of a reaction container 20b for which a ultraviolet lamp 21 needs to be replaced and a position of a spare reaction container 20b are exchanged in a way that the two reaction containers 20b which are arranged to be opposite to each other with a rotational axis 30 as a center are rotated by an angle of 180 degrees around the rotational axis 30. Then, the reaction containers 20b are detached from the reaction system, and hereafter presser covers 31 are opened. Thence, a used ultraviolet lamp 21 is taken out, and is replaced with a brandnew lamp 21. Although a fixing mechanism for each ultraviolet lamp in the reaction container 20b is not illustrated, the mechanism is a combination of a spring and a screw. This enables the lamps 21 to be replaced with a simple motion. In this way, the replacement and removal of ultraviolet light can be performed without suspending the reaction even if the photolytical reaction device 4 is being operated. Moreover, in a mechanism to which a spare reaction container 20b is not provided (see Fig.4), while a ultraviolet lamp is being replaced, flons are not photolyzed. However, unreacted flons are fed back uninterruptedly into the photolytical reaction device 4 by the gases separating membrane 5. By this, lamps can be replaced without suspending the operation in this case, too.

[0034] An ultraviolet lamp in a conventional, open-type reaction container which is not illustrated is cooled by the air. A air cooling method is an open-type reaction container in which the air is forcedly flown into cavities among a plurality of ultraviolet lamps in the reaction container and into

intervals between the wall of the outer periphery of the reaction container and an ultraviolet lamp. For this reason, ultraviolet light is absorbed by the air (oxygen) which is used for air cooling, the air to be flown into the reaction container is consumed here. In addition, oxygen which absorbs ultraviolet light causes a photolytical reaction, and hereby part of the oxygen is transformed into oxygen atoms and a ozone. The air for air cooling which includes these oxygen atoms and the ozone is discharged to the outside, and the oxygen atoms and the ozone included in the discharged air are harmful to human bodies even though in a minute amount (ozone in an 8-hour working environment needs to be less than 0.1ppm). On the other hand, oxygen atoms and an ozone are useful chemical substances for accelerating decomposition of flons as long as they are in the reaction container.

[0035] Unlike the conventional, open-type reaction container, the photolytical reaction device 4 of a type in which ultraviolet lamps 21 are contained in the reaction container 20 as shown in Fig.4 does not include cavities for air-cooling ultraviolet lamps 21 in the reaction container 20 as a sealed-off type reaction container 20′ as shown in the figure. Ultraviolet lamps 21 are cooled by flons which are supplied for the reaction and the air which has been rid of moisture. This brings about the following advantages. Specifically,

① Oxygen atoms and an ozone which are harmful to human bodies even though in a minute amount are not emitted to the outside.

② Oxygen atoms and a ozone which have been produced in the course of cooling are used for the reaction for processing flons without losing them.

[0036] In a case of a photolytical reaction device 4 in which the section 20a of light source and the reaction container 20b are connected by the optical fiber 25 or the high reflecgtance mirror 26 as shown in Fig.5, a stop cock 33 is provided to the pathway of a mixed gas of the air and flons, which connects the section 20a of light source with the reaction container 20b. When a ultraviolet lamp 21 in the section 20a of light source is replaced, the aforementioned gas pathway 34 is shut off by the stop cock 33, and gas in the section 20a of light source is temporarily reserved in a gas reservoir 36 which is arranged in the section 20a of light source. After the used lamp 21 is detached outside the photoreaction system, when the section 20a of light source is again returned to a photolytical reaction system, the stop cock 33 of

the aforementioned gas pathway 34 and a stop cock 37 of the gas reservoir are opened so that an uninterrupted reaction is resumed.

[0037] The gases separating membrane 5

As described in detail in the previous invention for which a patent application has been filed by the present inventors, the gases separating membrane 5 according to this embodiment uses either of the followings.

(i) a silicon hollow fiber membrane (M-60 and M-80,manufactured by Nagayanagi, Inc.)

(ii) a polyimide hollow fiber membrane (UM-A1, manufactured by Ube Kosan, inc).

In an uninterrupted method according to this embodiment, a polyimide hollow fiber membrane had a higher capability of separating chlorine gases than that of a silicon hollow fiber membrane. In addition, when the temperature of the polyimide hollow fiber membrane is raised to approximately 150 degrees, the decomposition rate takes up a higher value. For this reason, it is preferable that a separating membrane which constructed of a polyimide hollow fiber membrane is used in a state that the membrane is being heated.

[0038] (7) The device 6 for recovering and reserving halogens

A chief product in the method for decomposing and recycling flons by use of ultraviolet light is a chlorine gas or bromine. The chlorine gas is industrially useful, but is harmful to human bodies (chlorine in an 8-hour working environment need to be less than 0.5ppm). For this reason, chlorine gas which has been separated from unreacted flons by the gases separating membrane 5 needs to be recovered and recycled safely and assuredly. The device 6 for recovering and reserving halogens according to this embodiment employs the same principle as a flons recovering device used for an automobile air conditioner does, by which halogens are caused to permeate through the gases separating membrane and a chlorine gas which has been separated from unreacted flons is recovered and reserved. In other words, a chlorine gas is compressed into a high temperature, high pressure gas by a compressor. The compressed halogen gas is cooled into liquid chlorine by a condenser. The chlorine is recovered and reserved in a cylinder in a liquid state. The reason why the principle of the flons recovering device for an automobile air conditioner can be adapted (the recovering device itself on a case-by-case basis) is that the boiling point of

CFC-12 which is refrigerants for an automobile air conditioner is substantially equal to that of chlorine.

[0039] The device 7 for separating and recovering fluorine containing powder.

Fluorine containing powder which is produced by polymerizing chemical reaction intermediates moves inside the device along with flowing gases. For this reason, a felt-like filter and a reservoir of fluorine containing powder which falls from the filter (the device for separating fluorine containing powder 7) are provided to the front of the gases separating membrane 5, and separate and recover fluorine containing powder from the flowing gases. In addition, a reservoir (not illustrated) of fallen fluorine containing powder is also arranged underneath the reaction container 20, and the fluorine containing powder is recovered.

[0040] A device for decomposing and recycling flons which are contained in foamed materials.

An annual amount of CFCs used for foamed materials is approximately 40,000 tons, and this amount sums up to 25% of a total amount of CFCs used annually in this country. According to the kinds of flons, approximately 2.5 tons of CFC-11, and approximately 1.2 tons of CFC-12 are used annually (actual figures in 1988). Flons contained in used foamed materials are emitted into the atmosphere if the used foamed materials are disposed of by doing such as crushing. If left as it is or disposed of in land reclamations, foamed materials gradually deteriorate, and accordingly flons are emitted into the atmosphere. For this reason, flons contained in used foamed materials need to be processed in order to make them harmless. Since used foamed materials are collected in small amounts and in separate manners, it is rational that processes for making flons contained in used formed materials harmless are carried out at each recovering service agents. Flons contained in used foamed materials are recovered in a following manner. The used foamed materials are compressed only by a pressing force generated by an electrical-hydraulic compressor at a temperature nearly equal to a room temperature, and hereby the flons are caused to be emitted. The flons are recovered into a container by a device for recovering flons. The recovered flons are introduced into the apparatus for decomposing and recycling flons by use of ultraviolet light, and are made harmless. In addition, the compressing of the foamed materials brings up an advantage of

reducing volumes of the very base components of the foamed materials.

[0041] As described above, according to this embodiment, refrigerants with which an electrical refrigerator, an automobile air conditioner, a household air conditioner and the like are filled in a small amount and separately are recovered. Flons and the like contained in the recovered refrigerants are decomposed easily, and are made harmless. In this way, processes for recycling are carried out. The system according to this embodiment is highly operable, since the system does not include steps for chemical processing, and since the system can be performed under conditions close to a room temperature and a normal pressure. In addition, the apparatus according to this embodiment can be provided as a movable and simple apparatus.

[0042]

[Effect of the Invention]

According to the present invention, a practical system for uninterruptedly decomposing and recycling flons and flon equivalents can be established. In addition, the system according to the present invention does not include steps of chemical processing, can perform processes under processing conditions close to a room temperature and a normal pressure, and is a system for uninterruptedly implementing processes. For this reason, the system is a highly operable, simple system.

[Brief Description of the Drawings]

[Fig.1] Fig.1 is a schematic view of a system for decomposing and recycling flons according to an embodiment of the present invention.

[Fig.2] Fig.2 is a reaction simulated model of an atom extraction reaction.

[Fig.3] Fig.3 is a view of a device for separating flons and lubricants completely according to the embodiment of the present invention.

[Fig.4] Fig.4 is a view of a photolytical reaction device according to the embodiment of the present invention.

[Fig.5] Fig.5 is a view of the photolytical reaction device according the embodiment of the present invention.

[Fig.6] Fig.6 is a view of the photolytical reaction device according to the embodiment of the present invention.

[Description of Reference numerals]

1 ... DEVICE FOR SEPARATING FLONS AND LUBRICANTS

2 ... DEVICE FOR SEPARATING MOISTURE COMPLETELY

3 ... AIR SUPPLYING DEVICE
4 ... PHOTOLYTICAL REACTION DEVICE
5 ... GASES SEPARATING MEMBRANE
6 ... DEVICE FOR RECOVERING AND RESERVING HALOGENATED GASES
7 ... DEVICE FOR SEPARATING AND RECOVERING FLUORINE CONTAINING POWDER
10 ... SEPARATOR
11 ... INTRODUCTION DUCT OF REFIGERANTS
12 ... FELT-LIKE FILTER
13 ... LUBRICANT RESERVOIR
15 ... BAFFLE BOARD
20 ... GLASS REACTION CONTAINER
20a ... SECTION OF LIGHT SOURCE
20b ... REACTION CONTAINER
21 ... ULTRAVIOLET LAMP
22 ... ULTRAVIOLET LIGHT REFLECTION MEMBRANE
23 ... ULTRAVIOLET LIGHT
24 ... CONDENSER LENS
25 ... OPTICAL FIBER CABLE
26 ... HIGH REFLECTANCE MIRROR
27 ... CONNECTING TUBE
30 ... ROTATIONAL AXIS
34 ... GAS PATHWAY

Continued from the front page

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Fig. 1

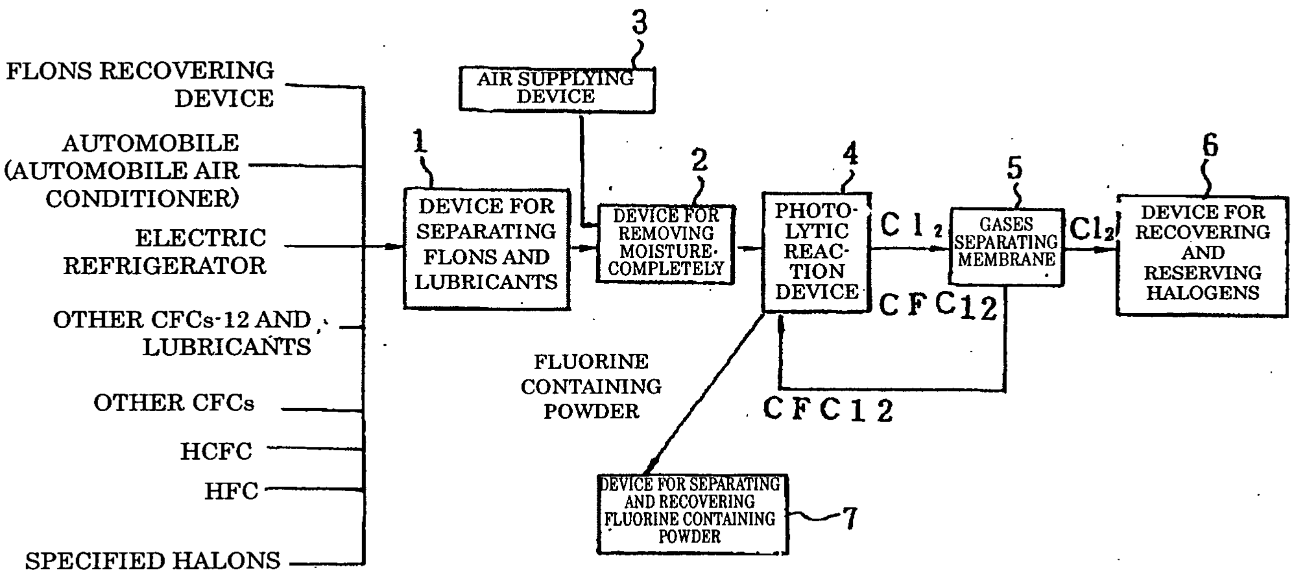
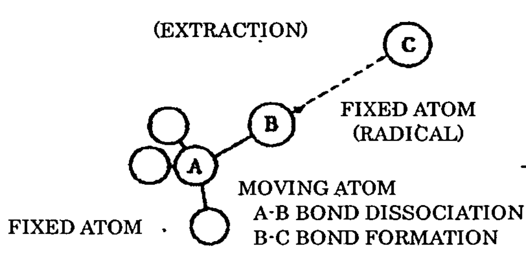


Fig. 2



SIMULATED MODEL OF EXTRACTION REACTION

Fig. 3

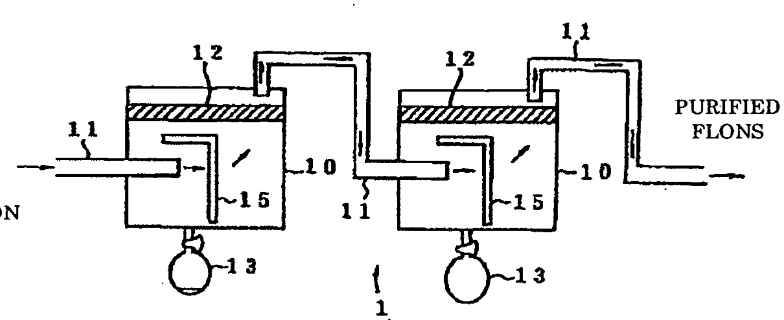


Fig. 4

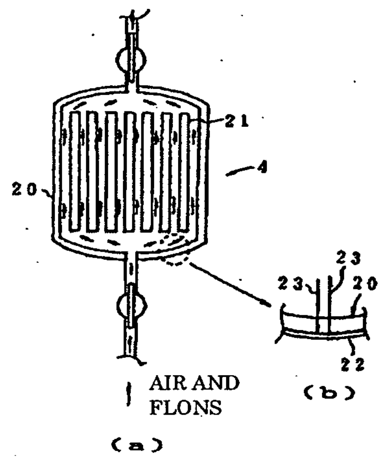


Fig. 5

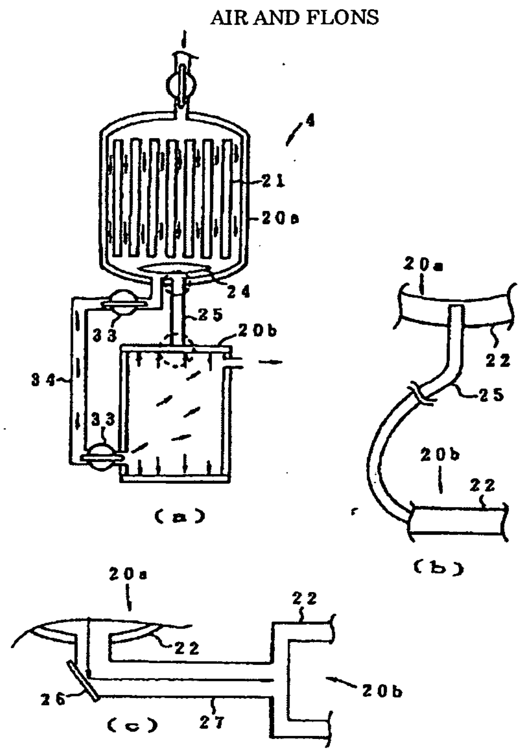


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Fig. 6